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㉙ **Selective epoxidation of olefins.**

㉚ Process is disclosed for the selective epoxidation of olefins having no allylic hydrogens. Such olefins are contacted with an oxygen-containing gas in the presence of a silver catalyst and an organic halide under defined reaction conditions, thereby selectively producing epoxides in good yield.

**EP 0 326 392 A1**

**Description****Selective Epoxidation of Olefins**

This invention relates to oxidation reactions. In one aspect, this invention relates to selective oxidation reactions for the production of epoxides from olefins.

**Background of the Invention**

Epoxides are highly reactive chemical compounds which, as a result of their reactivity, can be used in a wide variety of applications. Unfortunately, due to the reactivity of epoxides, they are often difficult to prepare with high selectivity and in high yields. Ethylene is the only olefin which has been successfully oxidized employing molecular oxygen on a commercial scale to produce an epoxide.

Preferred catalysts employed for the oxidation of ethylene to produce ethylene oxide comprise silver on solid supports. When such catalysts are employed for the oxidation of olefins having no longer chain lengths than ethylene, no epoxides are obtained, but instead various higher oxidation products (up to and including carbon dioxide and water) are obtained.

Alternate routes to epoxides other than ethylene oxide include the non-catalytic oxidation of olefins with peroxides. Such processes are not only uneconomical, but are also hazardous due to the large quantities of peroxide required for the desired conversion.

It would, therefore, be desirable to be able to catalytically oxidize olefins having longer chain lengths than ethylene to produce epoxides directly. Such processes would provide large quantities of highly reactive olefin derivatives which would find a wide range of uses, such as for example, as polymer cross-linking agents, as reactive chemical intermediates, as precursors for the production of organic solvents, and the like.

**Objects of the Invention**

An object of the present invention, therefore, is to provide a catalytic process for the selective oxidation of olefins having a longer chain length than ethylene to selectively produce epoxides in high yield.

This and other objects of the present invention will become apparent from inspection of the detailed description and appended claims which follow.

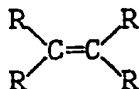
**Statement of the Invention**

In accordance with the present invention, we have discovered that olefins having no allylic hydrogens can be catalytically oxidized to produce a high selectivity of epoxide derivatives thereof by contacting the olefin feed with an oxygen-containing gas in the presence of a silver catalyst and, optionally, an organic halide, under defined oxidation conditions. The practice of the present invention makes possible the selective, large scale production of such highly functionalized compounds as butadiene oxide, t-butyl ethylene oxide, vinyl furan oxide, and methyl epoxy vinyl ketone, employing readily available feedstocks (e.g., butadiene, t-butylethylene, vinyl furan, and methyl vinyl ketone, respectively). The only other materials consumed during the invention reaction, besides the olefin feedstock, are molecular oxygen (and organic halide, when employed). Thus, the invention process is not only economical, but, since the reaction can be run in the continuous mode, it also makes possible the ready preparation of large quantities of these useful chemical compounds. In addition, carrying out the oxidation reaction in the presence of organic halide gives improved product yield, increased catalyst lifetime, and improved catalyst thermal stability.

**Detailed Description of the Invention**

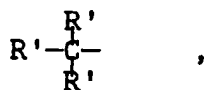
In accordance with the present invention, we have developed a process for the selective epoxidation of olefins having defined structure which comprises contacting the feed olefin with a sufficient quantity of an oxygen-containing gas so as to maintain the molar ratio of olefin to oxygen in the range of 0.01 up to 20, in the presence of a silver catalyst and, optionally, an organic halide, at a reaction pressure in the range of 0.1 up to 100 atmospheres and a temperature in the range of about 75 up to 325° C for a reaction time sufficient to obtain olefin conversions per pass in the range of about 0.1 up to 75 mole percent.

Olefins contemplated for use in the practice of the present invention are those which satisfy the following structural formula:



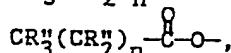
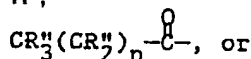
wherein each R is independently selected from:

- a) hydrogen,
- b) aryl and substituted aryl groups having in the range of 7 up to 20 carbon atoms,
- c) tertiary alkyl groups of the formula:



where each  $R'$  is independently:

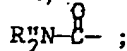
**R''.**



where R<sup>2</sup> is H, C<sub>1</sub>-C<sub>10</sub> alkyl or substituted alkyl, an aryl or substituted aryl group having 6 up to 20 carbon atoms, and n is a whole number from 0-12;

d)  $\text{CR}_3''-(\text{CR}_2'')_x-\text{O}-$ , where x is a whole number from 1-12;

e)



f)  $R_3N^-$  ;

g)  $R''S-$ ;

h)  $CR_2'' = CR'' - \langle CR'' = CR'' \rangle_y$ , where y is an integer from 0-20; or

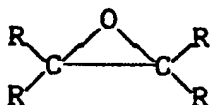


integer from 0-3,

where X is O, S or NR", and m is an integer from 0-3, with the proviso that said olefin have no allylic hydrogens and that at least one R-group not be hydrogen.

Exemplary olefins which satisfy the above structural formula include butadiene, tertiary butylethylene, vinyl furan, methyl vinyl ketone, N-vinyl pyrrolidone, and the like. A presently preferred olefin for the use in the practice of the present invention is butadiene because of its ready availability, relatively low cost, and the wide range of possible uses for the epoxide reaction produce.

The epoxides produced by the invention process have the structural formula:



wherein each R is independently defined as set forth above. Where one or more of the R-groups contain carbon-carbon bond unsaturation, further oxidation can be carried out in accordance with the present invention, thereby producing polyepoxide products.

The silver catalyst required for the practice of the present invention can be employed in either supported or unsupported forms.

When a support is employed, the loading level of silver on support typically falls within the range of about 0.1 up to 50 weight percent, calculated as elemental silver and based on the total weight of finished catalyst. Preferably, the loading level of silver on support falls within the range of about 1 up to 30 weight percent elemental silver; with loading levels in the range of about 2 up to 20 weight percent being most preferred.

It is presently preferred to apply the silver to a solid support for efficient use of the expensive silver component. Typical catalyst supports include

silica,  
alumina,  
silica-alumina,  
titanium oxide,  
lanthanum oxide,  
magnesium oxide,  
boron nitride.

boron carbide,  
 silicon nitride,  
 silicon carbide,  
 zinc oxide,  
 5 tin oxide,  
 iron oxide,  
 calcium oxide,  
 barium oxide,  
 strontium oxide,  
 10 zirconium oxide,  
 carbon,  
 boron phosphate,  
 zirconium phosphate,  
 and the like, as well as mixtures of any two or more thereof.

15 Typically, these solid supports will have a surface area of less than about 50 m<sup>2</sup>/g. Preferred supports will have a surface area of less than about 10 m<sup>2</sup>/g and will be neutral or moderately basic in character. The presently most preferred supports have surface areas of less than about 1 m<sup>2</sup>/g, and include alumina, silica, and silicon carbide.

20 The actual physical form of the catalyst support is not particularly important. While the form of the catalyst support has little effect on catalyst activity, practical considerations such as ease of heat transfer, mass transfer, pressure drop due to fluid flow restriction, efficiency of gas-liquid-solid contacting, catalyst durability, and the like make the use of defined shapes such as spheres, pellets, extrudates, rings, saddles, and the like preferred.

25 Especially preferred supports are those which have been treated with in the range of 0.001 up to 10 weight %, based on the total weight of catalyst, including support, of at least one promoter selected from:  
 the salts of alkali metal,  
 the oxides of alkali metals,  
 the salts of alkaline earth metals,  
 the oxides of alkaline earth metal,

30 organic halides,  
 inorganic halides,  
 acid halides, or  
 elemental halogens.

35 Exemplary salts of alkali metals include sodium nitrate, sodium sulfate, sodium chloride, sodium bromide, rubidium nitrate, rubidium acetate, lithium sulfate, lithium chloride, cesium nitrate, cesium chloride, cesium bromide, and the like; exemplary oxides of alkali metals include sodium oxide, sodium hydroxide, cesium oxide, cesium hydroxide, lithium oxide, lithium hydroxide, and the like; exemplary salts of alkaline earth metals include barium nitrate, barium acetate, calcium nitrate, calcium acetate, calcium chloride, and the like; exemplary oxides of alkaline earth metals including barium oxide, barium hydroxide, calcium oxide, calcium hydroxide, and the like; exemplary organic halides employed as catalyst promoter include carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, methylene chloride, methylene bromide, ethylene dibromide, ethylene dichloride, methyl chloride, methyl bromide, ethyl chloride, ethyl bromide, dichloropropane, dichloroethylene, trichloroethylene, vinyl chloride, chlorobenzene, bromobenzene,  $\alpha$ -chlorotoluene, 2-chlorotoluene, and the like; exemplary inorganic halides include HCl, HBr, and the like; exemplary acid halides include HOCl, HOBr and the like; and the elemental halogens include chlorine, bromine and iodine. Those of skill in the art recognize that the above-recited compounds are merely illustrative of the compounds which are useful as promoters in the practice of the present invention, and that many other compounds which fall within the generic categories set forth above can also be identified and would be expected to also impart enhanced activity and/or selectivity to the catalyst employed in the practice of the present invention.

50 Of the above compounds, the alkali metal halides are the most preferred as catalyst promoters, i.e., for treatment of catalyst prior to contacting with molecular oxygen and the olefin to be oxidized. Exemplary preferred alkali metal halides include cesium chloride, rubidium chloride, potassium chloride, sodium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide, and the like.

55 Those of skill in the art recognize that catalysts employed in the practice of the present invention can include additional components which may modify catalyst activity and/or selectivity. Such additives may be incorporated into the finished catalyst because their presence aids catalyst preparation, e.g., binders, die lubricants, and the like; or additives may be incorporated as extenders to reduce the cost of catalyst preparation; or additives may be incorporated to extend the operating ranges for reaction temperature and/or pressure; or additives may be incorporated to increase catalyst lifetime under reaction conditions and/or to modify the amounts of catalyst promoters employed to produce enhanced catalyst activity. It is recognized, of course, that some additives (e.g., cesium) are suitably employed in very low levels (i.e., milligrams of additive per gram of catalyst); while other additives (i.e., binders, diluents, and the like) are suitably employed at significantly higher levels (i.e., as a significant percentage of the total catalyst weight).

65 Supported catalysts can be prepared employing techniques well known to those of skill in the art, such as, for example, by precipitation of the active metals on the support, by impregnation, by coprecipitation of

support and active metals, by grinding together solid support and active metal(s) in particulate form; and the like. When a promoter is also present in the catalyst, the order in which it is incorporated into the catalyst is not critical, i.e., support can be contacted with a silver source, then promoter; or support can be contacted with promoter, then a silver source; or support can be contacted simultaneously with both promoter and a silver source; and other such variations.

Most any source of silver is suitable for use in preparing the catalyst employed in the practice of the present invention. Since a preferred method for preparation of supported catalyst involves impregnation of support with a solution of a silver compound, soluble silver compounds are a presently preferred source of silver. Exemplary compounds are silver nitrate, silver oxalate, silver acetate, and the like. Those of skill in the art recognize that certain organic silver compounds require the addition of ammonia or an amine in order to solubilize the organic silver compound in aqueous medium; thus, the use of such solvation-promoting additives is contemplated in the practice of the present invention.

The process of the present invention is carried out by contacting the olefin to be oxidized with molecular oxygen and, optionally, an organic halide under oxidation conditions, i.e., in the presence of sufficient quantities of an oxygen-containing gas to provide a molar ratio of olefin to oxygen in the range of about 0.01 up to 20, and in the presence of 0 up to about 1000 parts per million (by volume of total feed) of organic halide. When employed, preferred quantities of organic halide for use in the practice of this optional embodiment of the present invention fall within the range of about 1 up to 100 parts per million, by volume of total feed.

While greater or lesser quantities of molecular oxygen can be employed, sufficient quantities of oxygen should be provided to insure that undesirably low levels of olefin conversion do not occur, while excessively high oxygen concentrations should be avoided to prevent the formation of explosive mixtures. Similarly, lower levels of organic halide will provide negligible effect on catalyst performance, while higher levels of organic halide would not be expected to provide any significant improvement in catalyst performance.

Suitable oxygen-containing gases include air, oxygen-enriched air, substantially purified oxygen, oxygen diluted with inert gases such as N<sub>2</sub>, Ar, CO<sub>2</sub>, or CH<sub>4</sub>, and the like.

Organic halides contemplated by the optional co-feed embodiment of the present invention include compounds of the structure R<sup>m</sup>X, wherein R<sup>m</sup> is a hydrocarbyl radical or halogenated hydrocarbyl radical having in the range of 1 up to 8 carbon atoms, and X is any one of the halogens, preferably chlorine or bromine, and wherein R<sup>m</sup> contains at least one hydrogen atom which is sufficiently acidic so as to render R<sup>m</sup>X capable of undergoing dehydrohalogenation under the reaction conditions. Exemplary organic halides include C<sub>1</sub> compounds such as methyl chloride, methyl bromide, methylene chloride, methylene bromide, chloroform and bromoform, and the like; C<sub>2</sub> compounds such as ethyl chloride, ethyl bromide, dichloroethane, dibromoethane, vinyl chloride, dichloroethylene, trichloroethylene, and the like; C<sub>3</sub> compounds such as dichloropropane, dibromopropane, dichloropropene, dibromopropene, and the like; C<sub>4</sub> compounds such as chlorobutane, bromobutane, dichlorobutane, dibromobutane, chlorobutene, bromobutene, dichlorobutene, dibromobutene, and the like; C<sub>5</sub> compounds such as mono-, di-, tri-, tetra- and pentachloropentanes or pentenes, mono-, di-, tri-, tetra-, and pentabromopentanes or pentenes, cyclopentylchloride, cyclopentylbromide, and the like; C<sub>6</sub> compounds such as mono-, di-, tri-, tetra-, penta- and hexachlorohexanes or hexenes, mono-, di-, tri-, tetra-, penta- and hexabromohexanes or hexenes, cyclohexylchloride, cyclohexylbromide, chlorobenzene, bromobenzene, and the like; C<sub>7</sub> compounds such as chlorotoluene, bromotoluene, benzyl chloride, benzyl bromide, mono-, di-, tri-, tetra-, penta-, hexa- and heptachloroheptanes or heptenes, mono-, di-, tri-, tetra-, penta-, hexa-, and heptabromoheptanes or heptenes, chlorocycloheptane, bromocycloheptane, and the like; C<sub>8</sub> compounds such as mono-, di-, tri-, tetra-, penta-, hexa-, hepta- and octachlorooctanes or octenes, mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octabromooctanes or octenes, and the like; as well as mixtures of any two or more thereof.

When employed, the organic halide can be added to the oxidation reaction zone in a variety of ways. For example, it can be mixed with the olefin to be oxidized and/or the oxygen-containing gas prior to contacting with the catalyst, or the organic halide can be introduced to the reaction zone separately from the feed olefin and/or the oxygen-containing gas.

Suitable reaction temperatures fall within the range of about 75 up to 325°C. At lower temperatures, the reaction proceeds so slowly as to be impractical, while at higher temperatures undesirable levels of by-products, e.g., carbon dioxide, are obtained. Preferred reaction temperatures fall within the range of about 125 up to 275°C; with temperatures in the range of about 175 up to 250°C being most preferred because selectivity to the desired epoxide falls off at temperatures significantly about 250°C and space-time yields are undesirably low at temperatures below about 175°C.

The reaction pressure can vary within wide ranges, with typical limits of about 0.1 up to 100 atmospheres being chosen primarily as a function of safety, handling, equipment and other practical considerations. Preferably, reaction pressure is maintained in the range of about 1 up to 30 atmospheres.

Reaction times suitable for the practice of the present invention can vary within wide ranges. Generally, olefin, oxygen, organic halide and catalyst are maintained in contact for a time sufficient to obtain olefin conversions per pass in the range of about 0.1 up to 75 mole percent. Preferred target olefin conversion levels per pass fall within the range of about 1 up to 50 mole percent, while reaction times sufficient to obtain olefin conversion per pass in the range of about 5 up to 30 mole percent are presently most preferred for efficient utilization of the reactor capacity.

Those of skill in the art recognize that the actual contact times required to accomplish the desired

conversion levels can vary within wide ranges, depending on such factors as vessel size, olefin to oxygen ratios, the silver loading level on the catalyst, the presence or absence of any catalyst modifiers (and their loading levels), the amount of organic halide present in the reaction zone, the reaction temperature and pressure, and the like.

5 The invention process can be carried out in either batch or continuous mode. Continuous reaction is presently preferred since high reactor throughput and high purity product is obtained in this manner. The batch mode is satisfactorily employed when high volume of reactant throughput is not required, for example, for liquid phase reactions.

10 For continuous mode of reaction carried out in the gas phase, typical gas hourly space velocities (GHSV) fall within the range of about 100 up to 30,000 hr<sup>-1</sup>. GHSV in the range of about 200 up to 20,000 hr<sup>-1</sup> are preferred, with GHSV in the range of about 300 up to 10,000 hr<sup>-1</sup> being most preferred because under such conditions the most desirable combination of feed olefin conversion and product selectivities are obtained.

15 When continuous mode of reaction is carried out in the liquid phase, typical liquid hourly space velocities (LHSV) employed will give contact times analogous to that obtained at the GHSV values given above. Most preferably, LHSV employed will fall in a range so as to produce the most desirable combination of feed olefin conversion levels and high product selectivity.

20 Recovery of product produced in the practice of the present invention can readily be carried out employing techniques well known by those of skill in the art. For example, where reaction is carried out in the continuous mode, unreacted starting material is initially separated from reaction products; and the desired product then isolated from the resulting product mixture by distillation, crystallization, extraction, or the like. Since the selectivity to the desired epoxide product is generally quite high, there are only small amounts of undesired reaction products from which to isolate the desired product.

The invention will now be described in greater detail by reference to the following non-limiting examples.

#### 25 EXAMPLE 1 - Catalyst Preparation

Catalysts were typically prepared by impregnation of support with a solution of a silver compound (and optionally a promoter) in 0.5-2 volumes of solvent relative to the volume of support being treated.

30 Thus, for example, a 14.2% Ag (as determined by neutron activation analysis) on Al<sub>2</sub>O<sub>3</sub> support was prepared by dissolving 202.3 grams of Kodak silver nitrate in 500 mL of distilled water. Five hundred grams of calcined Al<sub>2</sub>O<sub>3</sub> 3/16" spheres (surface area 0.39 m<sup>2</sup>/g, total pore volume 0.36 cc(Hg)/gm, median pore diameter 5.4μ, packing density 0.94 g/cm<sup>3</sup>, crush strength 65.2 pounds, chemical composition (wt %): Al<sub>2</sub>O<sub>3</sub> - 86.1, SiO<sub>2</sub> - 11.8, Fe<sub>2</sub>O<sub>3</sub> - 0.2, TiO<sub>2</sub> - 0.1, CaO - 0.4, MgO - 0.4, Na<sub>2</sub>O - 0.4, K<sub>2</sub>O - 0.6) were added to the silver-containing solution, the mixture tumbled for 30 minutes at 50°C, then water removed under vacuum at 60°C. The resulting pellets were then dried for 30 minutes at 120°C in a forced air oven. This material could be 35 calcined and used directly for oxidation of olefin feed or treated with a promoter and then calcined.

40 Prior to catalyst evaluation (and either before or after further treatment with promoter), all catalysts were optionally calcined in an oxygen-containing atmosphere (air or oxygen-supplemented helium) at about 350°C for about 4 hours. Following calcination, all catalysts employed in the following examples were subjected to an activation treated at a temperature in the range of about 300-350°C in an atmosphere initially containing about 2-5% hydrogen in an inert carrier such as helium or nitrogen. The hydrogen content of the activating atmosphere was gradually increased up to a final hydrogen concentration of about 20-25% at a controlled rate so that the activation temperature did not exceed 350°C. After the temperature was maintained for about 1 hour at a hydrogen concentration in the range of about 20-25%, catalyst was ready for use.

45 When a Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was treated with promoter, a quantity of catalyst was contacted with 0.5-2 volumes of aqueous promoter, then dried as previously described. In this way, the catalysts summarized in Table I were prepared. Unless otherwise noted in the Table, catalyst support employed was a fluidizable powder having a surface area of 0.26 m<sup>2</sup>/g, a total pore volume of 0.675 cc (Hg)/gm, median pore diameter 19μ, a packing density of 0.98 g/cm<sup>3</sup>, and a chemical composition (wt %) as follows: Al<sub>2</sub>O<sub>3</sub> - 84.7, SiO<sub>2</sub> - 13.4, Fe<sub>2</sub>O<sub>3</sub> - 0.21, TiO<sub>2</sub> - 0.47, CaO - 0.21, MgO - 0.12, Na<sub>2</sub>O - 0.15, K<sub>2</sub>O - 0.26:

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Table I  
Alumina-Supported Catalysts

<u>Catalyst</u>	<u>Silver loading, wt % (silver source)</u>	<u>Support</u>	<u>Promoter loading, mg/g* (Promoter Source)</u>
A	1.1 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0
A'	5.3 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0
B	15.2 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (pellets) <sup>1</sup>	0
B'	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	0
B''	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (rings) <sup>3</sup>	0
C	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0
D	19 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0
E	38 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0
F	5 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0 (CsCl)
G	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>4</sup>	1.0 (CsCl)
H	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0 (CsCl)

Table I (Cont'd.)

## Alumina-Supported Catalysts

<u>Catalyst</u>	<u>Silver loading,</u> <u>wt %</u> <u>(silver source)</u>	<u>Support</u>	<u>Promoter loading,</u> <u>mg/g*</u> <u>(Promoter Source)</u>
I	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.25 (CsCl)
J	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.50 (CsCl)
K	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0/0.024 (CsCl/Br <sub>2</sub> )**
L	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0/0.056 (CsCl/Br <sub>2</sub> )**
M	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0/0.12 (CsCl/Br <sub>2</sub> )**
N	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0/0.24 (CsCl/Br <sub>2</sub> )**
O	15 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (spheres) <sup>2</sup>	1.0/0.24 (CsCl/Br <sub>2</sub> + H <sub>2</sub> O)***
P	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.0 (CsCl)
Q	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0.44 (KCl)
R	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.33 (KCl)
S	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.42 (RbCl)



Table I (Cont'd.)  
Alumina-Supported Catalysts

<u>Catalyst</u>	<u>Silver loading, wt % (silver source)</u>	<u>Support</u>	<u>Promoter loading, mg/g* (Promoter Source)</u>
T	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0.36 (RbCl)
U	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	3.1 (Ba(NO <sub>3</sub> ) <sub>2</sub> )
V	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.45 (BaCl <sub>2</sub> )
W	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	0.24 (Br <sub>2</sub> )**
X	17 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.76 (RbNO <sub>3</sub> )
Y	18.9 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.0 (CsCl)
Z	18.9 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.26 (CsBr)
AA	18.9 (AgNO <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub>	1.16 (CsNO <sub>3</sub> )
BB	19 (Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub> )	Al <sub>2</sub> O <sub>3</sub>	0

Table I (Cont'd.)

## Alumina-Supported Catalysts

- \*milligram of promoter (based on weight of promoter compound) per gram of silver-treated support.
- \*\*prepared by dissolving elemental Br<sub>2</sub> in carbon tetrachloride (CCl<sub>4</sub>), then the Br<sub>2</sub>-CCl<sub>4</sub> solution was added to support which had previously been treated with silver and promoter (if employed); after mixing, then soaking for about 30 minutes, the CCl<sub>4</sub> was removed by evaporation on a rotary evaporator, and finally catalyst was calcined and reduced as described above.
- \*\*\*As in \*\* above, Br<sub>2</sub> was dissolved in CCl<sub>4</sub>, then enough water added to produce a two-phase system, which was then added to the previously Ag- and Cs-treated support; after soaking for about 30 minutes, catalyst was dried, calcined and reduced as described above.
- 13/16" pellets with a surface area of 0.26 m<sup>2</sup>/g, a total pore volume of 0.23 cc(Hg)/gm, median pore diameter of 19μ, a packing density of 0.90 g/cm<sup>3</sup>, and a chemical composition (wt %) as follows: alumina - 84.7, SiO<sub>2</sub> - 13.4, Fe<sub>2</sub>O<sub>3</sub> - 0.21, TiO<sub>2</sub> - 0.47, CaO - 0.21, MgO - 0.12, Na<sub>2</sub>O - 0.15, K<sub>2</sub>O - 0.26.
- 23/16" spheres with a surface area of 0.39 m<sup>2</sup>/g, a total pore volume of 0.36 cc(Hg)/gm, median pore diameter of 5.4μ, a packing density of 0.94 g/cm<sup>3</sup> and a chemical composition (wt %) as follows: Al<sub>2</sub>O<sub>3</sub> - 86.1, SiO<sub>2</sub> - 11.8, Fe<sub>2</sub>O<sub>3</sub> - 0.2, TiO<sub>2</sub> - 0.1, CaO - 0.4, MgO - 0.4, Na<sub>2</sub>O - 0.4, K<sub>2</sub>O - 0.6.

Table I (Cont'd.)  
Alumina-Supported Catalysts

$3\frac{1}{4}$ " rings having a surface area of  $0.43 \text{ m}^2/\text{g}$ , a total pore volume of  $0.37 \text{ cc (Hg)/gm}$ , a median pore diameter of  $7\mu$ , a packing density of  $0.80 \text{ g/cm}^3$ , and a chemical composition (wt %) as follows:  $\text{Al}_2\text{O}_3$  - 93.1,  $\text{SiO}_2$  - 5.6,  $\text{Fe}_2\text{O}_3$  - 0.3,  $\text{TiO}_2$  - 0.1,  $\text{CaO}$  - 0.1,  $\text{MgO}$  - 0.3,  $\text{Na}_2\text{O}$  - 0.1,  $\text{K}_2\text{O}$  - 0.1.

$4\frac{3}{16}$ " spheres having a surface area of  $0.13 \text{ m}^2/\text{g}$ , a total pore volume of  $0.37 \text{ cc (Hg)/gm}$ , a median pore diameter of  $32.5\mu$ , a packing density of  $0.88 \text{ g/cm}^3$ , and a chemical composition (wt %) as follows:  $\text{Al}_2\text{O}_3$  - 85.0,  $\text{SiO}_2$  - 12.0, and the remaining 3% as  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

Silver was deposited on other supports as well, following the same general procedure as above. Thus, 8.00% Ag on ZnO was prepared by dissolving 0.26 g of AgNO<sub>3</sub> in 10 mL of distilled water, then adding to the solution 2 g of uncalcined ZnO (having a surface area of 3.9 m<sup>2</sup>/g, and a particle diameter in the range of about 75-150μ). This material was then dried as described above and is designated as Catalyst CC.

5 Titania supported catalyst was prepared by calcining TiO<sub>2</sub> (having a surface area of about 0.5 m<sup>2</sup>/g, a particle diameter in the range of about 40-75μ) in oxygen at 450° for about 4 hours. Three grams of this treated TiO<sub>2</sub> was then slurried in about 10 mL of distilled water, to which was added a solution of about 10 mL of distilled water containing 73 mg of AgNO<sub>3</sub>. The combination was thoroughly mixed, then dried as described above. The resulting catalyst, containing about 1.9% Ag, is designated as Catalyst DD.

10 A higher silver loading-titania supporting catalyst was prepared by slurrying 3 g of TiO<sub>2</sub> calcined as described above in 15 mL of distilled water, then slowly adding to the slurry a solution of 0.26 g of AgNO<sub>3</sub> in about 10 mL of distilled water. The mixture was heated for about 1 hour to 80-90° C, then enough formaldehyde was added dropwise until no further silver was precipitated upon addition of HCl to an aliquot of the supernatant liquid. The resulting catalyst had a silver loading of 5.2% and is designated Catalyst EE.

15 A calcium oxide supporting catalyst was prepared by adding 2.0 g of calcined CaO to 10 mL of distilled water in which was dissolved 0.26 g of silver nitrate. The mixture was warmed to ~50° C for ~1 hour, then water was removed under reduced pressure on a rotary evaporator at a temperature of about 60-70° C, and the sample then dried by placing in a forced air oven at 120° C for 1 hour. The resulting catalyst is referred to as Catalyst FF.

20 A silica-supported catalyst was prepared as per the general procedure set forth above using a silica support having a surface area of 0.18 m<sup>2</sup>/g, and a particle diameter in the range of 75-250μ. The resulting catalyst had a silver loading of 5 wt % and is designated as Catalyst GG.

A barium oxide supported catalyst was prepared as per the general procedure set forth above using a barium oxide support having a surface area of about 1 m<sup>2</sup>/g, and a particle diameter in the range of about 40-75μ. The resulting catalyst had a silver loading of 6.3 wt % and is designated as Catalyst HH.

25 Boron nitride (BN; Catalyst II), silicon nitride (Si<sub>3</sub>N<sub>4</sub>; Catalyst JJ) and silicon carbide (SiC; Catalyst KK) supported catalysts were prepared in accordance with the standard procedure set forth above. In each case, support was contacted with the necessary amount of aqueous silver nitrate to achieve a 5 wt % Ag on support catalyst. After soaking for about 30 minutes, water was removed on a rotary evaporator, catalyst dried in a forced air oven at 120° C, then catalyst loaded into a reactor for in situ activation, which consisted of calcination for 4 hrs. at 350° C in a stream of 20% O<sub>2</sub>/80% He, followed by reduction for 1 hr. at 350° C in a stream of 20% H<sub>2</sub>/80% He. The catalyst designations, supports used and support properties are summarized below.

Support (surface area)	Resulting 5 wt % Ag catalyst
BN (2.9)	II
Si <sub>3</sub> N <sub>4</sub> (11.9)	JJ
SiC (0.12)	KK

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#### EXAMPLE 2 - Effect of Silver Loading Level

In all of the following catalyst evaluation runs, catalysts were evaluated under steady state conditions in a 1 atmosphere, single-pass flow reactor system. The reactor tube was constructed of pyrex and the catalyst charge (between 0.1 and 20.0 g) was held in place by means of a pyrex frit. The geometries of the reactor and catalyst particles as well as bed depth were chosen to maintain and measure the true kinetic and catalytic aspects of the reaction. Gas hourly space velocities for all experiments fell within the range of about 200 up to 3000 hr<sup>-1</sup>. A chromel/alumel thermocouple sheathed in stainless steel was embedded within the catalyst bed to measure the true reaction temperature.

50 The feed gases C<sub>4</sub>H<sub>6</sub> and O<sub>2</sub>, as well as the diluent He, were added using mass flow controllers, which permitted highly accurate and reproducible flow rates of C<sub>4</sub>H<sub>6</sub>, O<sub>2</sub>, and He regardless of pressure changes from the supply cylinders or the reactor system downstream from the controllers.

Reaction product analyses (as well as feed composition analyses) were made using an in-line gas sampling loop connected directly to the inlet of a Varian 3760 gas chromatograph. Both thermal conductivity (TC) and flame ionization (FI) detectors [(connected in series below the packed Chromosorb 101 column (8 ft. by 2mm id pyrex capillary column)] were used to analyze all of the reaction products. The TC detector gave quantitative analyses for O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O and HCHO (if present), while the FI detector was used for organic molecules such as C<sub>4</sub>H<sub>6</sub>, butadiene monoxide, crotonaldehyde, 2,5-dihydrofuran, furan and acrolein. In practice, however, usually only the selective epoxidation product and olefin feedstock were present as organic molecules.

60 Further, by means of a switching valve, it was possible to divert the feed stream through the in-line sample loop prior to passage over the catalyst. In this way, quantitative analysis of the feed stream and comparison to the corresponding data from the reactor effluent were possible, thereby providing very accurate measurements of both conversion levels and product selectivities. Output from both the TC and FI detectors were integrated using computing integrators which were programmed to give both absolute quantities and rates of formation.

65 All reactor exit lines were heated and maintained at 125-140° C to prevent product condensation.

The GC analysis was performed using the following temperature programming schedule: an initial temperature of 100°C was held for 5 minutes, followed by a temperature program rate of +10°C/min up to a final temperature of 200°C which was then held for 7 minutes. The helium GC carrier rate was 20 mL/min.

In this example, the effect of silver loading level on feed olefin conversion and product selectivity (based on the moles of olefin converted) was investigated. Reaction parameters and results are presented in Table 2.

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Table 2

Catalyst	Reaction Parameters			C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity %***
	Temp, °C	Gas Feed** (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow (in mL (STP)/min)		
Ag powder	225	0:1:1	17.6	0.25	70
Ag <sub>2</sub> O*	225	0:1:1	17.6	0.01	60
A (1.1% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	20	0.8	68
A' (5% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	20	1.5	74
B (15% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18	2.4	67
B' (15% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.6	1.4	68
B'' (15% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	16.6	1.8	71
C (17% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.5	2.6	75
C (17% Ag on Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.5	1.1	88
D (19% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	17.4	2.5	81

Table 2 (Cont'd)

<u>Catalyst</u>	<u>Reaction Parameters</u>			<u>C<sub>4</sub>H<sub>6</sub> Conversion, %</u>	<u>Product Selectivity %***</u>
	<u>Temp, °C</u>	<u>Gas Feed** (He/O<sub>2</sub>/C<sub>4</sub>H<sub>6</sub>)</u>	<u>Total Gas Flow (in mL (STP)/min)</u>		
E (38% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.8	2.7	89

\*Grade 1 Ag<sub>2</sub>O powder was used as obtained from the supplier, activated by heating at 350°C in flowing hydrogen. The temperature was maintained at about 350°C by initially introducing 5% H<sub>2</sub> in He, with the hydrogen content gradually increased to about 20% (remainder He), and conditions of 20% H<sub>2</sub>/80% He and 350°C maintained for one hour before reactant feed commenced.

\*\*Volumetric ratio

\*\*\*Product selectivity is reported as selectivity to epoxide based on the moles of olefin converted.

The above results demonstrate that high catalyst activity and selectivity are obtained with both unsupported silver, and supported silver catalysts over a wide range of loading levels. As one might expect, higher activities are obtained at higher silver loading levels. It is of note that selectivity is not adversely affected even at increasing butadiene conversion levels.

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**EXAMPLE 3 - Effect of Adding Promoters**

A series of catalyst evaluations were carried out employing the same experimental setup described in Example 2. A variety of promoted catalysts were tested, with reaction parameters and results set forth in Table 3.

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Table 3

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
A (1.1% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	20	0.8	68	
A + 1.0 mg (CsCl per g. catalyst	250	0:1:1	20	10.0	96	
F ((CsCl)-5% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	20	4.5	94	
	250	0:1:1	20	9.5	88	
B' (15% Ag/Al <sub>2</sub> O <sub>3</sub> spheres)	225	0:1:1	21.0	0.5	87	
	250	0:1:1	18.6	1.4	68	
H ((CsCl)-15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	20	15	93	
	250	0:1:1	20	23	89	
G ((CsCl)-15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	20	9.4	94	
I ((CsCl)-15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.2	9.8	93	
	225	0:1:1	40.5	9.5	95	
	225	0:1:1	82.2	9.2	95	
	250	0:1:1	18.2	16	95	

Table 3 (Cont'd)

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
J ((CsCl)-15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	16.1		7.7	93
	225	0:1:1	35.5		7.3	95
	240	0:1:1	35.5		11.3	93
	250	0:1:1	16.1		11.5	90
K ((CsCl & Br <sub>2</sub> )- 15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	17.4		10	94
	225	0:1:1	38.0		9.9	95
	240	0:1:1	38.0		14	93
	250	0:1:1	17.4		14	90
L ((CsCl & Br <sub>2</sub> )- 15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	17.1		10.5	94
	225	0:1:1	38.0		9.8	95
	250	0:1:1	17.1		16	93

Table 3 (Cont'd)

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
M ((CsCl & Br <sub>2</sub> )- 15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	17.6		8	94
	225	0:1:1	39.0		7.2	96
	240	0:1:1	39.0		11.8	94
	240	0:1:1	55.0		11.1	94
	250	0:1:1	17.6		12	91
N ((CsCl & Br <sub>2</sub> )- 15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	16.5		6.8	93
	225	0:1:1	36.8		6.4	95
	240	0:1:1	36.8		10.3	93
	250	0:1:1	16.5		11.3	89

Table 3 (Cont'd)

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
O ((CsCl & Br <sub>2</sub> )- 15% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	17.2		4.4	90
	225	0:1:1	36.4		4.0	93
	240	0:1:1	36.4		7.5	90
	240	4:1:1	56.6		7.3	87
	240	0:1:1	70.6		7.1	93
	240	2:1:1	72.3		7.6	90
	240	1:1:1	80.0		8.3	92
	250	0:1:1	17.2		8	85
C (17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.5		1.1	88
	250	0:1:1	18.5		2.6	75
P (CsCl-17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.0		5.5	97
	250	0:1:1	18.0		11	96

Table 3 (Cont'd)

	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
Q (KCl-17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.9		0.2	96
	250	0:1:1	18.9		0.5	74
R (KCl-17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.6		0.1	98
	250	0:1:1	18.6		0.4	75
S (RbCl-17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.4		2.4	95
	250	0:1:1	18.4		5.5	89
T (RbCl-17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.7		0.1	96
	250	0:1:1	18.7		0.3	67
U (Ba(NO <sub>3</sub> ) <sub>2</sub> - 17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.3		0.8	90
	250	0:1:1	18.3		1.7	76
V (BaCl <sub>2</sub> - 17% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.4		0.3	83

Table 3 (Cont'd)

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp, °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
W (Br <sub>2</sub> -17% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.2		0.2	73
X (RbNO <sub>3</sub> -17% Ag/Al <sub>2</sub> O <sub>3</sub> )	225	0:1:1	18.4		4.5	92
	250	0:1:1	18.4		9.9	86
D (19% Ag on Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	17.4		2.5	81
Y (CsCl-19% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	17.5		15.1	94
Z (CsBr-19% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	18.2		5.0	96
AA (CsNO <sub>3</sub> -19% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	16.5		15	77

\*\*\*Product selectivity is reported as selectivity to epoxide based on the moles of olefin converted.

These results demonstrate that alkali metal and alkaline earth metal compounds increase the rate of butadiene monoxide formation and/or increase the selectivity to the desired product (relative to that obtained with unpromoted catalyst), with both rate and selectivity frequently being improved. The addition of halogens is also shown to be an effective means to increase the selectivity to butadiene monoxide.

The benefit of these additives is observed to be independent of the silver loading and the nature of the support employed.

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#### EXAMPLE 4 - Effect of Various Catalyst Supports

A series of catalyst evaluations were carried out employing the same experimental setup described in Example 2. A variety of supported catalysts, prepared using different catalyst supports, were tested. The reaction parameters and results are set forth in Table 4.

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Table 4

Catalyst	Reaction Parameters				C <sub>4</sub> H <sub>6</sub> Conversion, %	Product Selectivity, %***
	Temp. °C	Gas Feed (He/O <sub>2</sub> /C <sub>4</sub> H <sub>6</sub> )	Total Gas Flow in mL (STP)/min			
A' (5% Ag/Al <sub>2</sub> O <sub>3</sub> )	250	0:1:1	20		1.5	74
CC (8.0% Ag/ZnO)	250	0:1:1	19.7		0.2	70
DD (1.9% Ag/TiO <sub>2</sub> )	225	0:1:1	20		0.06	60
EE (5.2% Ag/TiO <sub>2</sub> )	225	0:1:1	18.3		0.03	53
FF (5% Ag/CaO)	250	0:1:1	19.0		0.2	47
GG (5% Ag/SiO <sub>2</sub> )	250	0:1:1	20		1.1	87
HH (6.3% Ag/BaO)	250	0:1:1	20		0.1	87
II (5% Ag/BN)	200	0:1:1	20		0.2	68
	225	0:1:1	20		0.8	61
JJ (5% Ag/Si <sub>3</sub> N <sub>4</sub> )	225	0:1:1	20		0.1	66
	275	0:1:1	20		0.9	38
KK (5% Ag/SiC)	225	0:1:1	20		0.1	70
	275	0:1:1	20		0.9	61

\*\*\*Product selectivity is reported as selectivity to epoxide based on the moles of olefin converted.



These results demonstrate that a variety of supports are effective for the highly selective conversion of butadiene to butadiene monoxide. The results also indicate that alumina and silica are the presently preferred supports for use in the practice of the present invention.

EXAMPLE 5 - Selective Epoxidation of a Variety of Olefins

The same experimental set-up described in Example 2 was employed with t-butylethylene as the olefin feed and 1.77 g of Catalyst P (see Table 1). Reaction parameters and results are set forth in Table 5.

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Table 5  
t-Butylethylene (TBE) Oxidation

Reaction Temp., °C	Gas Feed (He/TBE/O <sub>2</sub> )	Total Gas Flow in mL (STP)/min	TBE Conversion, %	Product* Selectivity, %***
250	25/1/25	10	0.6	41
250	20/1/20	10	0.2	>95
250	85/1/85	6	1.0	>95
250	200/1/200	6	1.5	>95
275	60/1/60	6	1.9	43
275	25/1/25	6	1.1	34

\*Desired product is t-butylethylene monoxide.

\*\*\*Product selectivity is reported as selectivity to epoxide based on the moles of olefin converted.

These results demonstrate that olefins having no allylic hydrogens, e.g., t-butyl ethylene, can be selectively oxidized to the mono-epoxide derivative according to the practice of the present invention.

#### EXAMPLE 6 - Effect of Organic Halide Co-Feed

The effect of the optional use of organic halide co-feeds such as 1,2-dichloroethane on the conversion of butadiene to butadiene monoxide over a promoted, supported silver catalyst was investigated.

For these reactions, a new catalyst was prepared by dissolving 132 g of silver nitrate (Kodak) in 300 mL of distilled water. To this solution was added 500 g of 1/4" diameter  $\text{Al}_2\text{O}_3$  rings (see Table I, footnote 3). The mixture was tumbled for 30 minutes at about 50°C, then the bulk water removed under reduced pressure at about 60°C. The resulting, preliminarily dried rings were then further dried, while being slowly tumbled for about two hours at 170°C in a forced air oven. The silver weight loading was determined by neutron activation analysis to be about 12 wt %. The resulting material was then calcined as described in Example 1.

After calcination, a portion of the silver-treated alumina was promoted by adding 200 g of the calcined catalyst to a solution of 224 mg CsCl and 32 mg  $\text{CsNO}_3$  in 120 mL of methanol. The rings were agitated in the methanol solution for about five minutes, then the bulk methanol was removed by rotary evaporation. The promoted catalyst was dried as described above at 170°C in a forced air oven, and then activated in a hydrogen-containing atmosphere as described in Example 1. The resulting catalyst is composed of 12 wt % Ag/ $\text{Al}_2\text{O}_3$  promoted with 1.12 mg CsCl/g catalyst and 0.16 mg  $\text{CsNO}_3$ /g catalyst (for a total promoter level of 0.99 mg Cs/g catalyst and 0.235 mg Cl/g catalyst. This catalyst is designated as Catalyst LL.

In similar fashion, Catalyst MM was prepared having a silver loading level of 12 wt % on alumina rings and promoted with 0.79 mg Cs/g catalyst and 0.21 mg Cl/g catalyst.

The oxidation of butadiene was then carried out using Catalysts LL or MM according to the procedure set out in Example 2. In addition, organic halide was added via a mass flow controller which delivered a gas stream containing 100 parts per million (by volume) of organic halide (helium diluent) to the reactant feed stream. By proper selection of flow rate for the 100 ppm organic halide-containing feed as diluted into the helium/olefin/oxygen feed stream, it was possible to very accurately and reproducibly control the level of organic halide in the process feed stream.

Table 6 illustrates the controlled and reversible effects of co-feeding an organic halide such as 1,2-dichloroethane to a reaction zone employed for the selective oxidation of butadiene to butadiene monoxide. The data are presented in the order in which the experiments were conducted. Reaction product analyses were conducted after about 60 minutes exposure to each concentration of dichloroethane.

Table 6

Catalyst Activity (Catalyst MM) at 250°C for  
Oxidation of Butadiene to Butadiene Monoxide\*

<u>Feed Concentration of 1,2-Dichlo- roethane, ppm</u>	<u>% Butadiene Conversion</u>	<u>% Selectivity, Butadiene Monoxide</u>
0	20.4	90.8
20	16.2	91.0
5	19.3	91.0
10	17.5	92.0
0	21.0	91.0

\*Feed gas ratios:  $\text{He/butadiene/O}_2 = 4/1/1$ ; gas  
hourly space velocity was about 600  $\text{hr}^{-1}$ .

The results in Table 6 demonstrate that the effect of organic halide on catalyst performance is reversible. Another series of reactions were carried out with dichloroethane co-feed to determine the effect on product selectivity of long-term exposure of catalyst to organic halide co-feed.

Table 7

Product Selectivity for Butadiene Oxidation at  
250°C with Catalyst LL with Dichloroethane  
Co-Feed\*

5

	<u>Elapsed Time**</u>	<u>% Butadiene Conversion</u>	<u>% Selectivity, Butadiene Monoxide</u>
10	0	22.8	93.3
	18	20.6	93.4
	40	18.6	94.3
	90	16.3	94.8
15	113	15.2	94.8
	161	13.6	95.1

\*Feed gas ratios: He/butadiene/O<sub>2</sub> = 4/1/1; gas  
hourly space velocity was about 600 hr<sup>-1</sup>.

20 \*\*Measured in minutes after introduction of 20  
ppm dichloroethane was commenced.

The results in Table 7 demonstrate that organic halide co-feed causes an increase in selectivity to the  
desired epoxide product.

25 In order to demonstrate the stabilizing effect of organic halide co-feed on catalyst performance, two series  
of runs were carried out using Catalyst LL at a target reaction temperature of 228°C - one reaction modified by  
the addition of 1,2-dichloroethane co-feed and the other carried out in the absence of co-feed. A fresh sample  
of Catalyst LL was used for each series of runs. Results are set forth in Table 8.

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Table 8

Effect of Organic Halide Co-feed  
on Catalyst Stability\*

## A. No Organic Halide Co-feed

Time on Stream, min (Rxn. Temp, °C)**	% Conversion		% Selectivity, Butadiene Monoxide
	Butadiene	Oxygen	
51	6.4	5.1	96.9
76	9.0	5.7	97.8
101	11.0	7.1	97.5
126	11.6	7.5	97.6
154	12.7	8.4	97.3
187	13.3	8.9	97.1
211	13.4	8.9	97.2
240	13.7	9.3	96.8
262 (230)	14.1	9.4	97.1
284 (231)	14.4	9.6	97.1
307 (233)	15.3	10.4	96.9
328 (236)	16.5	11.6	96.4
349 (239)	17.1	12.2	96.2
375 (243)	18.5	14.5	94.7
401 (256)	21.5	22.7	89.3
420 (313)	16.8	60.8	39.8
441 (402)	12.1	92.0	6.7
460 (422)	11.2	92.1	1.4

## B. Co-feed of 4 ppm 1,2-dichloroethane (introduced after 270 minutes on stream)

Time on Stream, min.	% Conversion		% Selectivity, Butadiene Monoxide
	Butadiene	Oxygen	
73	7.4	4.6	97.9
103	9.4	5.9	97.8
128	11.5	6.3	97.6
157	12.9	7.7	97.3
180	13.6	8.8	97.3
243	14.7	10.4	96.4
266***	14.9	10.4	96.4
292	14.3	10.0	96.5
324	14.9	10.5	96.3
351	14.9	10.5	96.3
377	14.8	10.4	96.4

Table 8 (Cont'd.)

5	Time on Stream, min.	% Conversion		% Selectivity, Butadiene Monoxide
		Butadiene	Oxygen	
	404	15.0	10.8	96.2
	436	14.6	10.3	96.3
10	464	15.0	10.7	96.2
	491	15.2	10.7	96.3
	514	14.8	10.0	96.9
	537	15.2	10.5	96.7

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\*Feed gas ratios He/butadiene/O<sub>2</sub> = 4/1/1; gas hourly space velocity was about 2200 hr<sup>-1</sup>

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\*\*Reaction temperature was 228°C unless noted otherwise; temperature excursions are due to exothermic reaction resulting from uncontrolled rates of reaction.

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\*\*\*Organic halide co-feed commenced at 270 minutes on stream.

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The results in Table 8A illustrate the problem of catalyst instability over an extended reaction period. After several hours on stream, the temperature of the catalyst bed begins to increase dramatically. As the temperature of the catalyst bed increased, it was not possible to maintain the catalyst bed at the desired temperature, due to uncontrolled rate of reaction. In addition, selectivity to the desired epoxide product falls off dramatically.

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In contrast, the results in Table 8B demonstrate the stabilizing effect exerted by organic halide co-feed. Catalyst performance is maintained essentially constant over many hours of reaction, still performing at good conversion levels and at very high selectivities about nine hours after reaction was commenced. Note also that at the low level of organic halide employed (4 ppm), the steady state levels of conversion/selectivity obtained without added organic halide (See Table 8A; butadiene conversion about 13%, selectivity to epoxide about 97%) are maintained essentially unchanged (see Table 8B) in the presence of organic halide. Thus, it is apparent that a concentration of organic halide co-feed can be selected so as to maintain virtually any desired steady state level of catalytic activity.

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Another series of reactions were carried out to demonstrate the effect of a variety of organic halide co-feeds on the activity of supported silver catalysts used for the oxidation of butadiene to butadiene monoxide. For all the runs summarized in Table 9, reaction temperature was 225°C, feed composition was He/butadiene/O<sub>2</sub> = 4/1/1, gas hourly space velocity was about 2200 hr<sup>-1</sup>, and the catalyst employed was Catalyst LL.

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Table 9

Effects of Various Organic Halides on Catalytic Activity and Selectivity to Butadiene Monoxide

<u>Run No.</u>	<u>Organic Halide,* ppm</u>	<u>Elapsed time, min.</u>	<u>% Butadiene Conversion</u>	<u>% Selectivity, Butadiene Monoxide</u>
1	—	0	12.3	97.9
	DCP, 5	22	10.3	98.2
	DCP, 5	44	10.1	98.4
	—	67	12.4	97.8
	—	85	13.3	97.5
2	—	0	13.3	97.5
	DCM, 30	23	12.6	97.6
	DCM, 30	46	12.4	97.7
	—	63	13.9	97.7
	—	80	14.5	97.5
3	—	0	14.5	97.5
	MC, 30	17	14.3	97.4
	MC, 30	39	14.2	97.3
	—	56	14.7	97.2
4	—	0	15.4	96.3
	TCE, 2.5	18	11.8	97.8
	TCE, 2.5	37	11.0	97.9
	—	61	13.4	97.3
	—	84	14.6	97.5
5	—	0	14.6	97.5
	DCE, 2.5	14	13.9	97.5
	DCE, 2.5	37	14.0	97.4
	—	57	15.1	97.3
	—	75	15.3	97.1
6	—	0	15.3	97.1
	VC, 30	33	14.7	97.0
	—	38	15.7	96.9
7	—	0	14.0	96.3
	VB, 5	34	12.0	96.9
	—	57	12.9	96.5
	—	112	13.7	96.3
8	—	0	13.7	96.3
	EB, 5	10	7.3	97.8
	—	38	12.7	96.5
	—	95	13.4	96.2

Table 9 (Cont'd)

Run No.	Organic Halide,* ppm	Elapsed time, min.	% Butadiene Conversion	% Selectivity, Butadiene Monoxide
9	—	0	13.4	96.2
10	DBE, 5	37	9.8	96.6
	DBE, 5	60	9.4	97.3
	—	82	10.8	96.5
	—	163	11.3	96.1

\*DCP = 1,2-dichloropropane  
 DCM = dichloromethane  
 MC = methyl chloride  
 TCE = trichloroethylene  
 DCE = 1,2-dichloroethylene  
 VC = vinyl chloride  
 VB = vinyl bromide  
 EB = ethyl bromide  
 DBE = 1,2-dibromoethane

For each organic halide investigated, the catalyst activity (butadiene conversion) and selectivity (molar % selectivity to butadiene monoxide) were established both before organic halide addition, and after organic halide co-feed has been stopped. Thus, the values presented above in Table 9 as "0" time points (designated by a "-") represent steady-state values for a given run immediately prior to introduction of organic halide co-feed. Conversion/selectivity values are recorded for one or two data points after organic halide co-feed was introduced. Then one or two data points are recorded after organic halide co-feed was stopped (also designated by a "-").

The return of conversion/selectivity values to their pre-co-feed values shortly after co-feed is removed is indicative of the reversible and controlled nature of the moderating effect of each of the tested co-feeds on catalyst performance. A decline in butadiene conversion and an increase in selectivity to butadiene monoxide during organic halide addition is indicative of the moderating effect of the organic halide co-feed.

#### EXAMPLE 7 - Comparative Oxidation Reactions

We attempted to repeat the oxidation of olefins higher than ethylene (such as propylene, 1-butene, 2-butene, etc.) as suggested by Brengle & Stewart in U.S. 2,709,173. In efforts to follow the teachings of the reference, catalyst composition (5% Ag/Al<sub>2</sub>O<sub>3</sub>) and reaction parameters as set forth in the reference were followed as closely as possible.

The reaction parameters employed and results obtained are set forth in Table 10.



Table 10

<u>Catalyst</u>	<u>Feed</u>	<u>Reaction Parameters</u>			<u>Feed Conversion %</u>	<u>Product Selectivity, CO<sub>2</sub></u>	<u>Epoxide</u>
		<u>Temp. °C</u>	<u>Gas Feed (He/O<sub>2</sub>/olefin)</u>	<u>Total Gas Flow In mL (STP)/min.</u>			
A'	Ethylene	250	3:1:1	25	12	53	47
A'	Propylene	250	3:1:1	24	7	92	0
A'	1-Butene	250	3:1:1	23	3	92	0
A'	2-Butene	250	3:1:1	52.2	2	98	0

These results confirm the suggestions of the literature, e.g., "Oxidation of butadiene with Ag<sub>2</sub>O at 551°K (278° C) by means of pulse technique gave only CO<sub>2</sub> and a small amount of acrylaldehyde." [Bull. Chem. Soc., Jap. 51, 3061-3062 (1978)], and "Silver and silver oxide catalysts, although suitable for the oxidation of ethylene to ethylene oxide, do not seem to be similarly effective for the oxidation of the four-carbon olefins." [Ind. and Eng. Chem., 44, 594-603 (1952)]. The data set forth in Table 10 demonstrate that propylene, 1-butene and 2-butene are converted almost exclusively to CO<sub>2</sub>, with no observable epoxide formation.

These data refute the suggestion by Brengle and Stewart that the "lower molecular weight hydrocarbon olefins in particular are adaptable to this invention [preparation of olefin oxides]. Those which are normally gaseous, such as ethylene, propene, butene-1, butene-2 and butadiene, for example, are more suitable, with ethylene being preferred." [See Col. 2, l. 64-68]. The data set forth above confirm the suggestions of the art, i.e., that silver catalyzed oxidation is effective only for the production of epoxide from ethylene.

The more recent disclosures of Rao in U.S. 4,429,055 and U.S. 4,474,977 are consistent with the suggestions of the above-cited prior art. Rao determined that among the lower olefins, only ethylene can be selectively directly epoxidized. When Rao carried out the oxidation of propylene, 1-butene and 1, 3-butadiene under epoxidation conditions, no epoxide product was observed. For example, propylene conversion was calculated to be 46.1% based on the content of oxygen in the feed, with the primary product formed being acrolein (28.8% selectivity). The only other products of propylene oxidation were CO<sub>2</sub> and H<sub>2</sub>O.

Similarly, when Rao evaluated the oxidation of 1, 3-butadiene, the observed products were furan, acrolein, dihydrofuran and trihydrofuran:

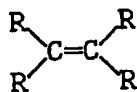
The selectivity to furan is 22.4% and to acrolein is 5.1%. Gas chromatographic analysis shows two other peaks besides furan and acrolein. They have retention times the same as a mixture of dihydrofuran and trihydrofuran.

See Col. 4 lines 1-5 of '997. Thus, Rao, consistently with all other relevant prior art, neither discloses nor suggests the selective formation of mono-epoxides from olefins such as butadiene, i.e., olefins having no allylic hydrogens.

The examples have been provided merely to illustrate the practice of our invention and should not be read so as to limit the scope of our invention or the appended claims in any way. Reasonable variations and modifications, not departing from the essence and spirit of our invention, are contemplated to be within the scope of patent protection desired and sought.

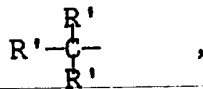
## Claims

1. A process for the selective epoxidation of olefins having the structure:

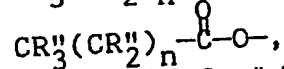
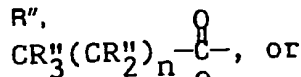


wherein each R is independently selected from:

- a) hydrogen,
- b) aryl and substituted aryl groups having in the range of 7 up to 20 carbon atoms,
- c) tertiary alkyl groups of formula:

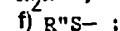
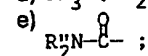


where each R' is independently:

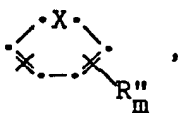


where R'' is H, C<sub>1</sub>-C<sub>10</sub> alkyl or substituted alkyl, an aryl or substituted aryl group having 6 up to 20 carbon atoms, and n is a whole number from 0-12;

d)  $\text{CR}_3''-(\text{CR}_2'')_x-\text{O}-$ , where x is a whole number from 1-12;



- g)  $R''S-$ ;  
 h)  $CR''_2=CR''-(CR''=CR'')_y$ , where y is an integer from 0-20; or



where X is O, S or  $NR''$ ; and m is an integer from 0-3,  
 with the proviso that said olefin have no allylic hydrogens and that at least one R-group not be hydrogen;  
 said process comprising contacting said olefin with a sufficient quantity of an oxygen-containing gas so  
 as to maintain the molar ratio of olefin to oxygen in the range of 0.01 up to 20, in the presence of a  
 silver-containing catalyst and from 0 up to 1000 ppm (by volume of total feed) of an organic halide having  
 the structure  $R''X$ , wherein  $R''$  is a hydrocarbyl or halogenated hydrocarbyl radical having in the range of 1  
 up to 8 carbon atoms, and X is any one of the halogens, at a pressure in the range of 0.1 up to 100  
 atmospheres, at a temperature in the range of 75 up to 325°C for a time sufficient to obtain olefin  
 conversions in the range of 0.1 up to 75%.

2. A process in accordance with Claim 1 wherein said silver catalyst is a supported silver catalyst  
 comprising in the range of 0.1 up to 75 weight % elemental silver.

3. A process in accordance with Claim 2 wherein said supported silver catalyst is supported on an  
 inorganic support having a surface area no greater than about 50 m<sup>2</sup>/g.

4. A process in accordance with claim 3 wherein said inorganic support is selected from:

silica,  
 alumina,  
 silica-alumina,  
 titanium oxide,  
 lanthanum oxide,  
 magnesium oxide,  
 boron nitride,  
 boron carbide,  
 silicon nitride,  
 silicon carbide,  
 zinc oxide,  
 tin oxide,  
 iron oxide,  
 calcium oxide,  
 barium oxide,  
 strontium oxide,  
 zirconium oxide,  
 carbon,  
 boron phosphate,  
 zirconium phosphate,  
 or mixtures of any two or more thereof.

5. A process in accordance with Claim 2 wherein said silver catalyst further comprises in the range of  
 0.001 up to 10 weight %, based on the total weight of catalyst, including support, of at least one promoter  
 selected from:

the salts of alkali metals,  
 the oxides of alkali metals,  
 the salts of alkaline earth metals,  
 the oxides of alkaline earth metals,  
 organic halides,  
 inorganic halides,  
 acid halides, or  
 elemental halogens,  
 as well as mixtures of any two or more thereof.

6. A process in accordance with Claim 5 wherein said promoter is a halide salt of an alkali metal or a  
 mixture of a halide salt and a nitrate salt of an alkali metal.

7. A process in accordance with Claim 1 wherein said olefin is selected from:

butadiene,  
 tertiarybutyl ethylene,  
 vinyl furan,

methyl vinyl ketone, or  
N-vinyl pyrrolidone,  
as well as mixtures of any two or more thereof.

5 8. A process in accordance with Claim 7 wherein said silver catalyst comprises:  
in the range of about 1 up to 30 weight % silver,  
in the range of about 0.001 up to 10 weight percent of an alkali metal halide and, optionally, alkali metal  
nitrate, and

an alumina support having a surface area of less than about 10 m<sup>2</sup>/g;  
wherein said weight percentages are based on the total weight of catalyst.

10 9. A process in accordance with Claim 7 wherein said silver catalyst comprises:  
in the range of about 2 up to 20 weight percent silver,  
in the range of 0.01 up to 2 weight percent of an alkali metal halide and, optionally, alkali metal nitrate,  
an alumina support having a surface area of less than about 1 m<sup>2</sup>/g;  
wherein said weight percentages are based on the total weight of catalyst.

15 10. A process in accordance with Claim 9 wherein said alkali metal salts are selected from cesium  
chloride, cesium bromide, or cesium nitrate.

11. A process in accordance with Claim 8 wherein said contacting is carried out at a temperature in the  
range of about 175 up to 250°C, at a pressure in the range of about 1 up to 30 atmospheres for a time  
sufficient to obtain olefin conversions in the range of about 1 up to 50%.

20 12. A process in accordance with Claim 9 wherein said contracting is carried out at a temperature in the  
range of about 175 up to 250°C, at a pressure in the range of about 1 up to 30 atmospheres for a time  
sufficient to obtain olefin conversions in the range of about 1 up to 50%.

13. A process in accordance with Claim 1 wherein said contracting is carried out in the presence of at  
least 0.1 ppm of said organic halide.

25 14. A process in accordance with Claim 13 wherein X is chlorine or bromine.

15. A process in accordance with Claim 14 wherein said organic halide is selected from:  
methyl chloride, methyl bromide, methylene chloride, methylene bromide, chloroform, bromoform, ethyl  
chloride, ethyl bromide, dichloroethane, dibromoethane, vinyl chloride, dichloroethylene, trichlo-  
roethylene, dichloropropane, dibromopropane, dichloropropene, dibromopropene, chlorobutane, bro-  
mobutane, dichlorobutane, dibromobutane, chlorobutene, bromobutene, dichlorobutene, dibromo-  
butene, mono-, di-, tri-, tetra- and pentachloropentanes or pentenes, mono-, di-, tri-, tetra- and  
pentabromopentanes or pentenes, cyclopentylchloride, cyclopentylbromide, mono-, di-, tri-, tetra-,  
penta- and hexachlorohexanes or hexenes, mono-, di-, tri-, tetra-, penta- and hexabromohexanes or  
hexenes, cyclohexylchloride, cyclohexylbromide, chlorobenzene, bromobenzene, chlorotoluene, bromo-  
toluene, benzyl chloride, benzyl bromide, mono-, di-, tri-, tetra-, penta-, hexa- and heptachloroheptanes  
or heptenes, mono-, di-, tri-, tetra-, penta-, hexa- and heptabromoheptanes or heptenes, chlorocyclohep-  
tane, bromocycloheptane, mono-, di-, tri-, tetra-, penta-, hexa-, hepta- and octachlorooctanes or octenes,  
mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octabromooctanes or octenes; as well as mixtures of any  
two or more thereof.

40 16. A process in accordance with Claim 13 wherein said organic halide is co-fed to the reaction zone in  
admixture with the olefin to be oxidized and/or the oxygen-containing gas.

17. A process in accordance with Claim 13 wherein said organic halide is fed to the reaction zone  
independently of the introduction of the olefin to be oxidized.

45 18. A process in accordance with Claim 1 wherein said oxygen-containing gas is selected from:

air,  
inert gas diluted air,  
inert gas diluted oxygen,  
oxygen-enriched air, or  
substantially purified oxygen.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89300776.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	<p>EP - A1 - 0 026 827 (EC ERDÖL-CHEMIE GMBH)</p> <p>* Claims 1,2; page 5, lines 19-25 *</p> <p>--</p>	1,4	<p>C 07 D 301/10</p> <p>C 07 D 303/04</p>
A	<p>EP - A2/A3 - 0 003 642 (IMPERIAL CHEMICAL INDUSTRIES LTD.)</p> <p>* Claims 1,2 *</p> <p>--</p>	1,18	
A	<p>FR - A - 2 523 971 (THE HALCON SD GROUP, INC.)</p> <p>* Claim 1 *</p> <p>--</p>	1,4,5	
A	<p>CHEMICAL ABSTRACTS, vol. 105, no. 24, December 15, 1986, Columbus, Ohio, USA</p> <p>GARFUNKEL, E.; DING, X.; DONG, G.; YANG, S.; HOU, X.; WANG, X.</p> <p>"The effect of sodium edlayers on the adsorption of oxygen on silver (100)"</p> <p>page 347, column 1, abstract no. 214 368m</p> <p>&amp; Chin. Phys. Lett. 1985, 2(9), 397-400</p> <p>--</p>	1	<p>TECHNICAL FIELDS SEARCHED (Int. Cl.4)</p> <p>C 07 D 301/00</p> <p>C 07 D 303/00</p>
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 24-04-1989	Examiner BRUS
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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89300776.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 102, no. 15, April 15, 1985, Columbus, Ohio, USA  CAMPBELL, CH.T.; PAFFETT, M.T. "The role of chlorine promoters in catalytic ethylene epoxidation over the silver (110) surface" page 572, column 1, abstract no. 131 377a  & Appl. Surf. Sci. 1984, 19(1-4), 28-42  -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 24-04-1989	Examiner BRUS
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	

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